

STUDIES ON FLUOROALKYL  
NITROSO COMPOUNDS

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## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vii
INTRODUCTION	1
DISCUSSION	9
A. Preparation of Fluoroalkyl Nitroso Compounds	9
B. Rate Studies of the Disproportionation of Some Fluorochloroalkyl Nitroso Compounds	17
C. Diels-Alder Addition of Some Fluoroalkyl Nitroso Compounds to Dienes	27
EXPERIMENTAL	38
A. Preparation of Mercury Alkyls	39
B. Reactions of Mercury Alkyls with Nitrosyl Chloride	44
C. Rate Studies of the Disproportionation of Nitroso Compounds	50
D. Reactions of Nitroso Compounds with Dienes	68
E. Miscellaneous Reactions	78

## TABLE OF CONTENTS (continued)

	Page
SUMMARY	80
BIBLIOGRAPHY	82
BIOGRAPHICAL SKETCH	85

# LIST OF TABLES

Table	Page
1. SUMMARY OF RATE CONSTANTS AND PRODUCT RATIOS FOR DISPROPORTIONATION OF NITROSO COMPOUNDS AT 78.2°	21
2. PROPERTIES AND ANALYSES OF NEW COMPOUNDS PREPARED	34
3. RATE OF DISPROPORTIONATION OF 1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 78.2°	53
4. RATE OF DISPROPORTIONATION OF 1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 78.2° IN THE PRESENCE OF ADDED NITROSYL CHLORIDE	55
5. RATE OF DISPROPORTIONATION OF 1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE IN THE PRESENCE OF ADDED NITRIC OXIDE	57
6. RATE OF DISPROPORTIONATION OF 1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 57.0°	59
7. RATE OF DISPROPORTIONATION OF 1-NITROSO-1,1-DICHLOROTRIFLUOROETHANE AT 78.2°	61

# LIST OF TABLES (continued)

Table	Page
8. RATE OF DISPROPORTIONATION OF 1-NITROSO- 1-CHLOROTETRAFLUOROETHANE AT 78.2°	63
9. RATE OF DISPROPORTIONATION OF 1-NITROSO- 2-CHLOROTETRAFLUOROETHANE AT 78.2°	65

## LIST OF FIGURES

Figure	Page
1. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane at 78.2°	54
2. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane (9.3 millimoles) at 78.2° in the presence of nitrosyl chloride (2.1 millimoles)	56
3. Concentration vs. time: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane ( <u>ca.</u> 1.1 millimoles) at 78.2° in the presence of nitric oxide ( <u>ca.</u> 0.7 millimole)	58
4. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane at 57.0°	60
5. First order plot: disproportionation of 1-nitroso- 1,1-dichlorotrifluoroethane at 78.2°	62
6. First order plot: disproportionation of 1-nitroso-1-chlorotetrafluoroethane at 78.2°	64
7. First order plot: disproportionation of 1-nitroso-2-chlorotetrafluoroethane at 78.2°	67

## INTRODUCTION

The requirements of modern technology for materials which can be subjected to extremes of temperature and still remain serviceable have become increasingly great over the past fifteen years. Recognizing these needs, the Office of the Quartermaster General established at the University of Florida and elsewhere in 1951 a program of research and development for the purpose of finding elastomeric materials which have a combination of thermal stability, low temperature flexibility and resistance to swelling in a variety of solvents.

Since some fluorine-containing materials, e.g., "Teflon," had demonstrated high chemical resistance and thermal stability, a worthwhile approach seemed to be the introduction of fluorine atoms into monomers. The presence of fluorine in an elastomer considerably improves its resistance to swelling in organic solvents. This is ascribed to the lower solubility of the fluorine-containing elastomer in the solvent.

Tarrant and Lovelace (36) began the research in this laboratory by synthesizing some fluorobutadienes. The method employed was the peroxide initiated addition of perhaloalkanes to



olefins, followed by dehydrohalogenation. Tarrant and Lilyquist (35), Tarrant and Gillman (34), Lutz (27) and others extended this work, preparing a wide variety of dienes containing fluorine.

Tomasino (39) prepared a number of unsaturated fluorine-containing silanes and siloxanes while Stump (32) prepared a variety of unsaturated fluoroethers.

More recently, considerable interest has been shown in fluoroalkyl nitroso compounds. The copolymers of these materials with fluoroolefins have low chain-stiffness and little chain-chain interaction due to the N-O linkage and to the absence of hydrogen (29). The copolymer of trifluoronitrosomethane and tetrafluoroethylene, containing the  $-\{N(CF_3)OCF_2CF_2\}_n$  repeating unit, has received the most attention and has been found to have good low temperature flexibility, high chemical resistance, to exhibit little tendency to swell in a variety of solvents and, in addition, it does not burn. These findings prompted a more thorough investigation of fluoroalkyl nitroso compounds.

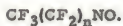
Nitroso compounds have been known for over eighty years. Baeyer (4,5) prepared the first examples, N,N-dimethyl-p-nitrosoaniline and nitrosobenzene, which he obtained from the reaction of nitrosyl chloride with diphenylmercury. During the next forty years major contributions to our understanding of these materials were

made and most of the preparative methods that are known today were first used during that time.

Much of the more recent research on nitroso compounds has been concerned with the refinement of our knowledge of these compounds, e. g., elucidation of the structure of the dimer which aliphatic nitroso compounds form, improvement of the theoretical treatment of the electronic transitions which result in absorption of visible and ultraviolet light etc., rather than with their preparation and reactions. However, the preparation of fluoroalkyl nitroso compounds is still a difficult task. Known preparative methods are few and limited in scope and only a few reactions have been investigated. Hence, the preparation and reactions of fluoroalkyl nitroso compounds are still of considerable interest. Finding new preparative methods and investigating some of the reactions of these materials were the major objectives of this research.

The first fluoroalkyl nitroso compound was prepared by Ruff and Geise (31). They obtained nitrosotrifluoromethane by treating silver cyanide (contaminated with silver nitrate) with fluorine. Several years later, Hasseldine (17, 18) and Banus (8) prepared nitrosotrifluoromethane from trifluoriodomethane and nitric oxide by irradiating a mixture of the two gases over mercury with ultraviolet light. Other perfluoroalkyl iodides were also reacted to obtain

several members of the series having the general formula,



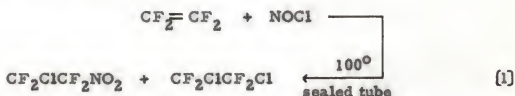
Although Haszeldine (21) and Mason, nee Banus (28) claim that yields are good, the experience of another worker in this laboratory has been that yields are poor. In preparing a 100-gram sample of nitrosotrifluoromethane, a series of half mole runs in a 22-liter flask were carried out. Each run required about 24 hours and yielded 7 to 8 grams of product, a yield of less than 20 per cent. Because the reaction is time consuming and the yields are poor, this is not a good preparative method.

Another method that has been successfully employed in the preparation of fluoroalkyl nitroso compounds is the addition of nitrosyl chloride to fluoroolefins. Park (30) has added nitrosyl chloride to fluoroolefins in a flow reactor packed with ferric chloride. However, difficulties were encountered due to blocking of the tube when the reaction was run on large scales. Tarrant and Pisacane (37) have overcome this difficulty by passing nitrosyl chloride and a fluoroolefin through a column containing aluminum chloride dissolved in dimethylformamide. This method appears to be easily adaptable to large scale preparations.

The addition of nitrosyl chloride to hydrocarbon olefins goes readily under very mild conditions and has been known for many

years (38). The reaction has been used widely in determining the structures of terpenes. However, while its application to the preparation of fluoroalkyl nitroso compounds is obvious, the experimental conditions to be employed are anything but obvious. The mechanism of addition to fluoroolefins is quite different from that of addition to hydrocarbon olefins. Fluoroolefins undergo nucleophilic attack whereas hydrocarbon olefins undergo electrophilic attack. Thus, there is no valid basis for expecting one type of olefin to undergo the ionic reactions of the other type.

Haszeldine (18) had also attempted the preparation of nitroso compounds by the addition of nitrosyl chloride to fluoroolefins, but under the conditions he employed (100° for several hours) the nitro and chloro\* compounds were formed. For example:



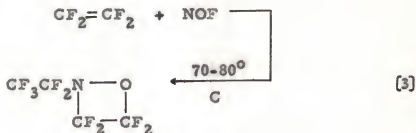
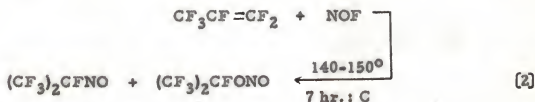
No doubt the nitroso compound was an intermediate in the reaction to form the nitro compound. Some pure halofluoroalkyl nitroso

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\* Throughout this dissertation the term chloro compound refers to the compound which results from replacing the nitroso group by a chlorine atom.

compounds yield similar products when heated. This reaction will be considered more fully in the Discussion section of this dissertation.

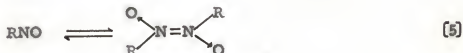
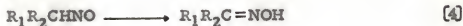
The addition of nitrosyl fluoride to fluoroolefins has also been attempted. Knunyants and co-workers (23) carried out the reaction using several fluoroolefins. With octafluoroisobutylene a 100 per cent yield of 2-trifluoromethyl-2-nitrosohexafluoropropane was obtained. Results were somewhat different with other olefins.



Yields were not given for any of the other reactions, leading one to suspect they were not very good. The conditions used in the two reactions illustrated above are essentially the same conditions under which nitrosotrifluoromethane undergoes disproportionation to the nitro and asoxy compounds (22). Haszeldine (10) and Andreades (1) have confirmed that nitrosyl fluoride and tetrafluoroethylene react to

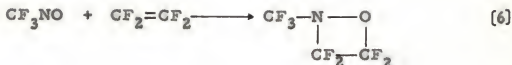
form the oxazetidine (equation [2] above), but Andreades obtained results from the addition of nitrosyl fluoride to other fluoroolefins which differed somewhat from the findings of Knunyants.

In some respects the fluoroalkyl nitroso compounds differ markedly from their hydrocarbon analogues. For example, in contrast to the aliphatic nitroso compounds which undergo one or both of the two reactions:



the fluoroalkyl nitroso compounds exist as the intensely blue monomers. Tautomerization to the oxime (equation [4] above) is, of course, not possible with the perhaloalkyl nitroso compounds since there are no  $\alpha$ -hydrogen atoms in the molecules. There is no evidence of dimerization (equation [5] above) even at  $-78^\circ$ . This is attributed to the strong inductive effect of the fluoroalkyl group which causes the nitrogen atom to be relatively electron deficient.

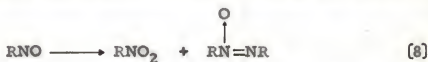
There are also many similarities between the reactions of fluoroalkyl nitroso compounds and those of the aliphatic and aromatic nitroso compounds. For example, Haszeldine (9) found that nitrosotrifluoromethane reacts with tetrafluoroethylene to yield the oxazetidine:



This result is in accord with the earlier results Ingold (20) obtained when he reacted aromatic nitroso compounds with hydrocarbon olefins:



The disproportionation which nitroso compounds undergo when heated (7):



is also characteristic of some fluoroalkyl nitroso compounds (22).

Nitroso compounds undergo a wide variety of reactions (15), many of which have not yet been extended to the fluorine-containing nitroso compounds. It seems certain that as better methods of synthesis of these materials are developed, chemists will make increased use of these materials as intermediates.

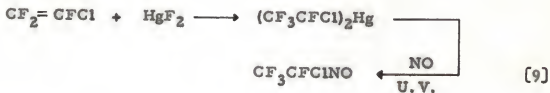


## DISCUSSION

### A. Preparation of Fluoroalkyl Nitroso Compounds

Among the most common and best starting materials for the synthesis of fluorine-containing materials are fluoroolefins. These materials are relatively inexpensive and a fairly wide variety of them, representing a wide range of reactivity, is available. It thus seemed worthwhile to seek reaction routes to fluoroalkyl nitroso compounds which used fluoroolefins as starting materials. Two such methods, the additions of nitrosyl chloride and nitrosyl fluoride to fluoroolefins, and their limitations were discussed in the Introduction section of this dissertation.

Fluoroalkyl mercury compounds seemed to offer a convenient route to nitroso compounds. Considering the chemical properties of mercury alkyls, either of the following two-step reactions might occur:







it appears that the reaction is limited to 1,1-difluoroolefins. All of the olefins which have been found to undergo the reaction are of this type, while two of the olefins which did not react, hexafluorocyclobutene and 2,3-dichlorohexafluorobutene-2, are internal olefins. This observation is consistent with the reactivity of fluoroolefins in other ionic additions. For example, the addition of sodium cyanide to fluoroolefins has been reported only for 1,1-difluoroolefins (14).

The reaction very probably proceeds by an initial attack of fluoride ion upon the fluoroolefin followed by addition of either mercuric ion or the species  $\text{HgF}^+$ . Fluoroolefins are known to undergo nucleophilic attack.

All of the mercury alkyls used in this work were volatile, white solids except bis-heptafluoroisopropylmercury which was a volatile liquid. The solids sublime readily at  $100^\circ$ , thus offering a convenient means for their purification. They are soluble in most organic solvents, but, except for bis-trifluoromethylmercury (13), are not very soluble in water. They are stable to aqueous acid solutions, but are decomposed readily by aqueous sodium hydroxide solutions.

The preparation of nitroso compounds from the mercury alkyls did not prove to be as simple a task as was first anticipated. Aliphatic mercury alkyls are known (12) to be good sources of free

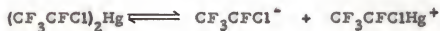
radicals, so it might be expected that irradiation of the fluoroalkyl mercury compounds with ultraviolet light in the presence of nitric oxide would result in the formation of nitroso compounds. Indeed, Hasseldine (18) had utilized the reaction of a free radical with nitric oxide to prepare some perfluoroalkyl nitroso compounds. With bis-(1-chlorotetrafluoroethyl)mercury the reaction proved to be much too slow to use as a preparative method. In one run a very faint blue color was noted after several days of irradiation, but this color disappeared within a day. An attempt was made to form the radicals thermally by passing a benzene solution of this mercury alkyl through a tube at 500° using nitric oxide as the atmosphere in the tube. The only product from this reaction was a material which was thought to be 2,3-dichlorooctafluorobutane, but which was not positively identified.

Since the free radical reaction had not worked, the obvious next step was to try the reaction of fluoroalkyl mercury compounds with nitrosyl chloride. This type of reaction was first used by Baeyer (4) in 1874 when he carried out the reaction of diphenylmercury with nitrosyl chloride and obtained nitrosobenzene.

This reaction proved successful with some of the mercury alkyls and 1-nitroso-1-chlorotetrafluoroethane, 2-nitrosoheptafluoropropane and 1-nitroso-1,1-dichlorotrifluoroethane were prepared by

this method. The only solvent in which the reaction proceeded at a reasonable rate at room temperature was dimethylformamide. Though the reaction seemed to proceed at a comparable rate in dimethyl sulfoxide, the yield of product was considerably lower. In diethylene glycol dimethyl ether (diglyme) the reaction was much too slow to be useful while in acetone and benzene the reaction apparently did not take place.

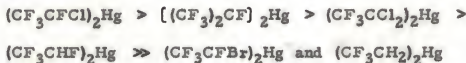
The great increase in reaction rate with increase in dielectric constant of the solvent seems to indicate that formation of a charged species is a factor in the overall rate. Either of the following reaction schemes is consistent with the experimental facts:



In equations [11], the rate of the second step should decrease slightly with increasing dielectric constant, but the rate of the first step would strongly increase with increasing dielectric constant. Therefore, the overall rate should increase with increasing dielectric constant. In equations [12], the slow step is the ionization of the

mercury alkyl, which would strongly increase with increasing dielectric constant. It is impossible to distinguish between the two on the basis of this experimental evidence.

The order of reactivity of the mercury alkyls with nitrosyl chloride is:



No nitroso compound was obtained from the reaction of either bis-(1-bromotetrafluoroethyl)mercury or bis-(2,2,2-trifluoroethyl)-mercury with nitrosyl chloride, while the following reaction was anomalous:



The expected 1-nitroso-1,2,2,2-tetrafluoroethane was not a product. Attempts to isolate additional products, such as  $\text{CF}_3\text{CF}=\text{N}-\text{OH}$ , which could account for the inability to isolate the expected product, proved unsuccessful. Since the yield of product was poor in this reaction it is difficult to tell what is happening, but it seems that the mercury alkyl must be chlorinated before it reacts to form a nitroso compound. The chlorination is very probably a free radical process in which a hydrogen atom is displaced by a chlorine atom. This seems more reasonable than an ionic process which would

involve either the displacement of a hydride ion or the attack of a chloronium ion to displace a proton.

The fact that 1-chloro-1,2,2,2-tetrafluoroethane is a minor product of the reaction is probably due to the displacement of mercury by a chlorine atom. Traces of mercury were noted in the reaction flask after the completion of one run. Furthermore, nitric oxide was found to be present in the product in all of these reactions. The most probable source of nitric oxide is the free radical cleavage of nitrosyl chloride. The chlorine atom would react while the nitric oxide would be a stable radical and would be swept over with the products.

In every case where reaction took place, the major product isolated was the nitroso compound. In each reaction, except the preparation of 2-nitrosoheptafluoropropane, some of the chloro compound\* was also obtained. This could arise either from the displacement of mercury by chlorine or from a subsequent decomposition of the nitroso compound by a free radical process. This second process will be discussed more fully later. The first mentioned possibility is more likely responsible for the formation

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\* As was noted in the Introduction, the term chloro compound refers to the compound which results from replacing the nitroso group by a chlorine atom.

of much of the chloro compound since the second process results in the formation of some nitro compound and only traces of nitro compounds were noted in two of the reactions while none was found in any of the others.

An additional product,  $(\text{CH}_3)_2\text{NH}_2^+ \text{HgCl}_3^-$ , was isolated from the reaction of bis-(1-chlorotetrafluoroethyl)mercury with nitrosyl chloride. It must arise from the interaction of nitrosyl chloride with the solvent and the mercuric chloride formed during the reaction. Although it was isolated and purified only in this particular reaction, it is very probably a product of all of the reactions of mercury alkyls with nitrosyl chloride in dimethylformamide. There was a solid present in all of the reaction flasks after they had stood for several days.

This two-step synthesis of nitroso compounds has limitations as a preparative method. However, it permits the preparation of certain fluoroalkyl nitroso compounds for which no other method is available. Furthermore, the reaction is of interest because it is apparently an ionic reaction of fluoroalkyl mercury compounds. This is the first ionic reaction of these materials to be reported.



B. Rate Studies of the Disproportionation of Some Fluorochloroalkyl Nitroso Compounds

In general, nitroso compounds do not exhibit great thermal stability. When fused, an aromatic nitroso compound disproportionates to an azoxy and a nitro compound (7). For example:



As was mentioned previously, certain perfluoroalkyl nitroso compounds also undergo this disproportionation when heated in the presence of activated charcoal at 100° for two days (22). Fluorochloroalkyl nitroso compounds having an  $\alpha$ -chlorine atom are even less stable. In the work discussed in this dissertation it has been found that certain chlorofluoroalkyl nitroso compounds have half-lives of the order of a few hours at 78.2° and the products of their disproportionation are somewhat different.

Workers who have attempted to prepare fluoroalkyl nitroso compounds by a reaction using nitrosyl chloride have frequently detected the presence of some chloro and nitro compounds (18, 30, 37). This has been attributed to the reaction of the nitroso compound with nitrosyl chloride (18). In this laboratory it was observed that certain fluorochloroalkyl nitroso compounds decomposed slightly on standing at room temperature for a few weeks. Also, in reactions between pure



nitroso compounds and various substrates significant quantities only of nitro and chloro compounds were obtained. These observations suggested that disproportionation according to equation [15]



R = fluorochloroalkyl

was occurring. To learn more about this reaction an investigation of the reaction kinetics and the nature of the products was undertaken.

The rates of disproportionation of four chlorofluoroalkyl nitroso compounds, 1-nitroso-1,2-dichlorotrifluoroethane, 1-nitroso-1,1-dichlorotrifluoroethane, 1-nitroso-1-chlorotetrafluoroethane and 1-nitroso-2-chlorotetrafluoroethane, were determined. These particular compounds were selected because of the location of the chlorine atoms.

The three nitroso compounds having an  $\alpha$ -chlorine showed first order rates of disproportionation over a range of about four half-lives. It cannot be said with certainty that 1-nitroso-2-chlorotetrafluoroethane follows a first order rate of disproportionation, but for purposes of comparison, it will be assumed to follow a first order rate. First order plots of the data obtained with both 1-nitroso-1,2-dichloro- and 1-nitroso-1,1-dichlorotrifluoroethane yield straight lines with very little deviation of the points. The first order plot of the data obtained with 1-nitroso-1-chlorotetrafluoroethane

yields a straight line, but there is considerable deviation of the points from the line, as is true of 1-nitroso-2-chlorotetrafluoroethane.

The fact that there is considerably more scattering of the points of the latter two compounds is very probably due to their being gases at room temperature, while the former two are liquids. Transferring aliquot portions of these materials to the reaction tubes was difficult and changes in the ratio of nitroso compound to internal standard are probably responsible for the scattering of the points. In spite of the scattering, useful information can be obtained from the data and valid comparisons of the rates can be drawn.

The nitro and chloro compounds account for the major portion of the nitroso compound that reacts. A more detailed study of the products of the disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane revealed that nitrogen and nitric oxide were both present in significant quantities, the nitrogen accounting for 20 per cent of the nitrogen originally present in the nitroso compound. There appeared to be a small amount of nitrosyl chloride present too, but there was no evidence that nitrous oxide was formed. In addition, a higher boiling material,  $C_7O_5NCl_3F_7$ , was also isolated. This material had absorption bands in the infrared at 5.49 and 5.62 microns and dissolved very slowly in distilled water to yield an acidic solution. This suggests that the material is an acid fluoride, but its structure is unknown.

The order of ease of disproportionation of the four nitroso compounds used in this study is:



It is apparent that the presence of an  $\alpha$ -chlorine greatly increases the rate of disproportionation.

Table 1 illustrates the differences in product distribution among the four compounds. It is significant that no chloro compound is obtained from 1-nitroso-2-chlorotetrafluoroethane whereas the chloro compound is a major product with each of the three  $\alpha$ -chloronitroso compounds.

The rate of disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane was also determined at 57.0°, so that the energy and entropy of activation could be calculated. The energy of activation was calculated from the equation:

$$\log (k_2/k_1) = (\Delta H_a/2.303R) [(T_2 - T_1)/T_2T_1]$$

where  $k_2$  and  $k_1$  are the rate constants at the temperatures,  $T_2$  and  $T_1$ ,  $T$  is expressed in degrees Kelvin,  $R$  is the gas constant and  $\Delta H_a$  is the energy of activation. The energy of activation was found to be 31 kcal./mole. The entropy of activation was calculated from the equation:

$$k = (kT/h)e^{\Delta S/R} e^{-\Delta H/RT}$$

TABLE 1

SUMMARY OF RATE CONSTANTS AND PRODUCT RATIOS FOR  
DISPROPORTIONATION OF NITROSO COMPOUNDS AT 78.2°

Compound	k (hr. <sup>-1</sup> )	t <sub>1/2</sub> (hr.)	RCI/RNO <sub>2</sub>	RCI + RNO <sub>2</sub> Average Percent Total Product
CF <sub>3</sub> CCl <sub>2</sub> NO	0.525	1.32	2.10	88
CF <sub>2</sub> CICFCINO	0.356	1.95	0.76	70
CF <sub>3</sub> CFCINO	0.173	4.00	1.14	62
CF <sub>2</sub> CICF <sub>2</sub> NO	0.0141	49.2	0.00	82
CF <sub>2</sub> CICFCINO + NOCl	0.485	1.43	0.74	107
CF <sub>2</sub> CICFCINO + NO	a	< 0.25	0.08 <sup>b</sup>	<u>ca.</u> 100

a. Could not be determined.

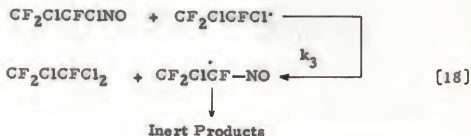
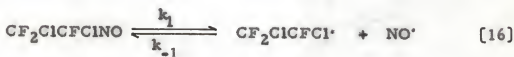
b. After one hour; ratio was smaller during earlier parts of the run.

where  $k$  is the rate constant in reciprocal seconds,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $T$  is the temperature in degrees Kelvin,  $\Delta H_a$  is the enthalpy of activation, and  $\Delta S$  is the entropy of activation. The assumption is made that:

$$\Delta H_a \approx \Delta H$$

The entropy of activation was found to be 12 cal./mole-deg.

It appears that the data can best be accounted for by the following reaction scheme, illustrated with 1-nitroso-1,2-dichlorotrifluoroethane:



The fact that the disproportionation follows first order kinetics eliminates the possibility that two molecules of nitroso compound react in some manner to form the nitro compound and an intermediate which

later forms the chloro compound. Such a reaction should follow second order kinetics.

The presence of nitric oxide among the products is evidence for a homolytic cleavage of the carbon-nitrogen bond. An attempt was made to inhibit the reaction by trapping the radicals formed with 2,6-di-tert-butylphenol, but the nitroso compound reacted very fast at room temperature with the inhibitor.

The extent of radical formation in equation [16], i.e., the relative magnitude of  $k_1$ , must be the rate controlling factor. Reaction [17] is fast when the concentration of nitric oxide is in the same range as that of the nitroso compound. This was shown by carrying out the disproportion of 1-nitroso-1,2-dichlorotrifluoroethane in the presence of added nitric oxide. Since the rate of disappearance of nitric oxide could not be followed, no rate constant for this reaction could be calculated. However, the half-life of the nitroso compound at  $78.2^\circ$  under the conditions of this reaction is less than 15 minutes compared with a half-life of the pure nitroso compound at  $78.2^\circ$  of almost 2 hours. Furthermore, the ratio of products is drastically changed. While the pure nitroso compound gives a ratio of  $RCI/RNO_2$  of about 0.75, the amount of chloro compound formed when nitric oxide is added is very small and the nitro compound accounts for practically all of the reacted nitroso compound. After the

reaction has proceeded 1 hour, the ratio goes up to 0.08. Less than the stoichiometric quantity of nitric oxide was used so the small amount of chloro compound formed is probably due to the disproportionation of the pure nitroso compound. This does not show that reaction [17] is much faster than reaction [16] under the conditions of the disproportionation of the pure nitroso compound, but it does show that there cannot be a large concentration of nitric oxide built up. This is also excellent evidence that nitric oxide is the species that oxidizes the nitroso compound to the nitro compound. Levy (26) reported the oxidation of nitrosomethane by nitric oxide, but gave no details; Brown (11) has reported the reaction of nitric oxide with isobutylene to yield a mixture of nitro compounds; and Bamberger (6) has reported that nitric oxide reacts with nitroso compounds to yield the diazonium nitrate. However, the mechanism of this oxidation is still rather obscure.

The rate of disproportionation is increased somewhat by the addition of nitrosyl chloride, but not nearly so much as by addition of nitric oxide. The addition of nitrosyl chloride did not change the ratio of  $\text{RCI}/\text{RNO}_2$ , but these two products account for all of the nitroso compound that reacts. Thus, it appears that reaction [18] is suppressed in favor of radical attack upon the chlorine in nitrosyl chloride.



Reaction [18] is suggested by the fact that each of the three  $\alpha$ -chloronitroso compounds yields the chloro compound as a major product while 1-nitroso-2-chlorotetrafluoroethane yields no chloro compound. It is difficult to say what the fate of the radical formed in this step might be. It might ultimately form the  $C_7O_5NCl_3F_7$  mentioned previously, either by reaction with more nitroso compound or by radical combination.

The factor controlling the extent of radical formation in equation [16] is probably the stability of the alkyl radical formed, that is, the energy difference between the nitroso compound and the two radicals. The smaller the energy difference the larger should be the ratio  $k_1/k_{-1}$ . Larger values of  $k_1/k_{-1}$  will result in larger concentrations of radicals and would thus increase the rate of reactions [17] and [18]. The reaction rates correlate very nicely with empirical observations on radical stability, which are that radical stability decreases in the order:



Stability of the radicals formed has been offered as the factor controlling direction of addition in free radical additions to fluoroolefins (19) using the above order of radical stability. The apparent resonance stabilization of  $CCl_3\cdot$  is greater than that of  $CF_3\cdot$  (40), so it is reasonable to expect the resonance stabilization of radicals to increase as chlorine is substituted for fluorine.



The much lower rate of disproportionation of 1-nitroso-2-chlorotetrafluoroethane is probably due to two factors: 1) The reduced resonance stabilization of  $\text{CF}_2\text{ClCF}_2\cdot$  compared with that of the  $\alpha$ -chloro radicals would shift the equilibrium in equation [16] to the left, thus decreasing the concentration of both nitric oxide and alkyl radicals; 2) There is no  $\alpha$ -chlorine for the alkyl radical to abstract. The alkyl radicals probably either react by combination or else react with the nitroso compound. Either reaction must be slower than halogen abstraction, since halogen abstraction occurs preferentially when an  $\alpha$ -chlorine atom is present. The rate at which alkyl radicals react to form products will affect the rate at which oxidation by nitric oxide occurs. However, the possibility that this compound disproportionates by an entirely different reaction route from that of the  $\alpha$ -chloro compounds cannot be discounted.

A possible reaction route by which these nitroso compounds disproportionate, which can be eliminated on the basis of the data obtained from these experiments is the following:



If reaction [19] were the initial step, then 1-nitroso-2-chlorotetrafluoroethane should disproportionate at a much faster rate than 1-nitroso-1-chlorotetrafluoroethane. Just the reverse is true.

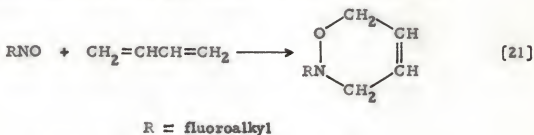
There is very little information in the literature concerning the disproportionation of nitroso compounds, although the reaction has been known for sixty years. It is, therefore, difficult to make comparisons between the reaction illustrated in equation [14] and the reaction discussed in this dissertation. It would be interesting to determine whether the disproportionation of the  $\alpha$ -chlorofluoroalkyl nitroso compounds is a phenomenon closely related to the general disproportionation shown in equation [14] or is a process which follows an entirely different reaction route. A kinetic investigation of the disproportionation of some aromatic nitroso compounds and some perfluoroalkyl nitroso compounds should reveal much.

#### C. Diels-Alder Addition of Fluoroalkyl Nitroso Compounds to Dienes

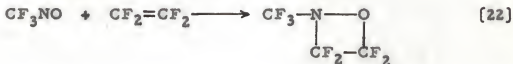
Nitroso compounds are known to undergo the Diels-Alder reaction with dienes to form oxazines (2, 3, 24, 41). It was of interest to extend this reaction to fluoroalkyl nitroso compounds to determine the effect of the fluoroalkyl group upon the reaction.

Nitrosotrifluoromethane, 1-nitroso-2-chlorotetrafluoroethane, 2-nitrosoheptafluoropropane, 1-nitroso-1,1-dichlorotrifluoroethane, 1-nitroso-1-chlorotetrafluoroethane and 1-nitroso-1,2-dichlorotrifluoroethane were reacted with butadiene, 1,1,2-trifluorobutadiene

and 1,1,3-trifluorobutadiene. The reactions were vigorous and usually went to completion within a minute or two at room temperature to give the oxazine as the only major product. For example:



In some of the reactions a small amount of a viscous, nonvolatile oil, which is probably a copolymer, was also obtained. No oxazetidines were isolated. Formation of the four-membered ring was a definite possibility since trifluoronitrosomethane reacts with certain fluoroolefins to form the oxazetidine (9):

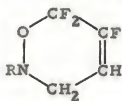


A proton nuclear magnetic resonance spectrum of the product shown in equation [21] had two absorption peaks in the methylene hydrogen region and two peaks in the vinyl hydrogen region, present in a ratio of 2:1, indicating the presence of only one double bond. One-four addition was confirmed by the absence of a characteristic vinyl group pattern.

The reactions of the nitroso compounds with 1,1,2-trifluorobutadiene similarly proceed by one-four addition. Each of the infrared

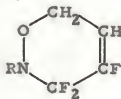
spectra of these adducts has a medium absorption band at 5.83 microns, the region in which  $-\text{CF}=\text{CH}-$  would be expected to absorb. The absence of a strong band at 5.55-5.60 microns precludes the presence of a trifluorovinyl group. Further, the absence of a band in the 6.00-6.10 micron region is evidence that a vinyl group is not present.

Addition to 1,1,2-trifluorobutadiene could occur in one or both of two directions to give the oxazines [23] and [24].



[23]

R = fluoroalkyl

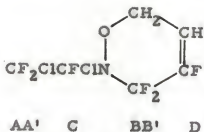


[24]

A detailed analysis\* by nuclear magnetic resonance of the product from the reaction between 1-nitroso-1,2-dichlorotrifluoroethane and 1,1,2-trifluorobutadiene showed the direction of addition to be that shown in [24] above. The analysis further indicated that the material was at least 95 per cent pure. The spectrum consisted of four groups of peaks, representing the four types of fluorine present. Peak assignments were made on the basis of chemical shifts and relative peak areas. The chemical shifts relative to trifluoroacetic acid are shown with structure [25]:

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\* This analysis was carried out by Dr. Wallace S. Brey, Jr., and his associates.



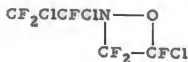
[25]

AA':  $\delta = -12.2$  p.p.m.      C:  $\delta = 30.2$  p.p.m.

BB':  $\delta = 20.3$  p.p.m.      D:  $\delta = 60.0$  p.p.m.

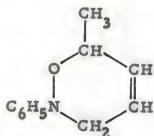
The preferred direction of addition is suggested by the magnitude of the coupling constants,  $J_{CB}$  and  $J_{CB'}$ , whose values are 37.0 c.p.s. and 14.2 c.p.s. These values are sufficiently large to eliminate from consideration the alternative structure ([23],  $R = CF_2ClCFCI-$ ). It is highly improbable that there would be any detectable coupling between B and C through both the nitrogen and oxygen atom. The spectrum is completely consistent with the structure shown in [25]. It is reasonable to assume that all of the additions to 1,1,2-trifluoro and 1,1,3-trifluorobutadiene proceed in a similar manner.

There is a similarity between the direction of addition in this reaction and that found in the reaction of 1-nitroso-1,2-dichlorotrifluoroethane with chlorotrifluoroethylene (16) to yield:



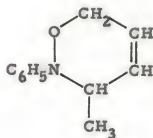
[26]

Arbuzov (3) found that nitrosobenzene and 1,3-pentadiene react to yield a mixture of:



[27]

and

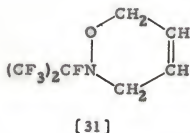
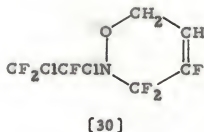
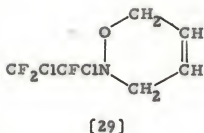


[28]

with structure [28] predominating. This result was cited as evidence of the radical nature of the Diels-Alder reaction, since an ionic mechanism should favor the formation of structure [27].

There was some variation of reaction rate with the structure of the nitroso compound. The reaction of 2-nitrosoheptafluoropropane with 1,1,2-trifluorobutadiene required a few hours at room temperature while the reactions of 1-nitroso-2-chlorotetrafluoroethane with butadiene and 1,1,2-trifluorobutadiene proceeded at  $-77^{\circ}$  as soon as the two reactants were mixed. The other reactions were intermediate between these two. Butadiene was somewhat more reactive than either of the trifluorobutadienes.

The stability of the products is noticeably influenced by the substituents on both the nitroso compound and the diene. For example,



structure [29] is rather unstable at room temperature while structure [30] is stable. Thus, the presence of fluorine atoms in the ring stabilizes the oxazine. Structure [31] is also stable at room temperature, which demonstrates that replacement of chlorine by fluorine in the alkyl group also increases the stability of the oxazine.

This is the first report of either 1,1,2-trifluoro- or 1,1,3-trifluorobutadiene undergoing the Diels-Alder reaction. Even excellent dienophiles like maleic anhydride do not react with these materials to form Diels-Alder adducts (33). It is thus apparent that nitroso compounds are extremely reactive dienophiles.

An attempt to add 1-nitroso-1,2-dichlorotrifluoroethane to perfluoroisoprene was unsuccessful; however, perfluoroisoprene is a very unreactive diene.

The physical properties and analyses of the new compounds prepared are tabulated in Table 2.



TABLE 2

PROPERTIES AND ANALYSES OF NEW COMPOUNDS PREPARED

Compound	B. P. (M. P.)	$n_D^{19}$	$d_4^{22}$	% Carbon		% Hydrogen		% Halogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CF_3CFBr)_2Hg$	(53-56°)	---	---	---	---	---	---	28.51	28.23 <sup>a</sup>
$(CF_3CCl_2)_2Hg$	(101-104°)	---	---	---	---	---	---	28.14	24.24 <sup>b</sup>
$[(CF_3)_2CF]_2Hg$	35°/26 mm.	---	---	13.40	0.00	0.00	49.50	42.83 <sup>c</sup>	
				14.24	0.94	0.94	42.83 <sup>c</sup>		
$CF_3CFCINO$	-5°	---	---	---	8.46	8.46	21.43	20.63 <sup>b</sup>	
				---	7.65 <sup>d</sup>	7.65 <sup>d</sup>	20.63 <sup>b</sup>		
$(CF_3)_2CFNO$	-13°	---	---	---	7.04	7.04	66.83	66.72 <sup>c</sup>	
				---	6.86 <sup>d</sup>	6.86 <sup>d</sup>	66.72 <sup>c</sup>		
$CF_3CCl_2NO$	36°	---	---	---	---	---	38.9	38.6 <sup>b</sup>	
				---	---	---	38.6 <sup>b</sup>		
$CF_2CICFCINOCH_2CH=CHCH_2$	67-68°/5 mm.	---	---	---	---	---	30.1	29.7 <sup>b</sup>	
				---	---	---	29.7 <sup>b</sup>		

TABLE 2 (continued)

Compound	B.P. (M.P.)	$n_D^{19}$	$d_4^{22}$	% Carbon		% Hydrogen		% Halogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CF}_2\text{ClCFClNOCH}_2\text{CH}=\text{CFCHF}_2$	35-36°/0.5 mm.	1.4016	1.643	24.85	24.71	1.04	1.25	---	---
$(\text{CF}_3)_2\text{CFNOCH}_2\text{CH}=\text{CHCH}_2$	24°/6 mm.	1.3602	1.476	33.23	33.30	2.39	2.56	---	---
$(\text{CF}_3)_2\text{CFNOCH}_2\text{CH}=\text{CFCHF}_2$	21-23°/1 mm.	1.3351	1.771	27.39	27.62	0.99	1.26	---	---
$\text{CF}_2\text{ClCF}_2\text{NOCH}_2\text{CH}=\text{CHCH}_2$	29°/3.5 mm.	1.4005	1.418	---	---	---	---	16.2	15.8 <sup>b</sup>
$\text{CF}_2\text{ClCF}_2\text{NOCH}_2\text{CH}=\text{CFCHF}_2$	36°/4 mm.	1.3632	1.610	26.35	26.49	1.10	1.23	---	---
$\text{CF}_3\text{CFClNOCH}_2\text{CH}=\text{CHCH}_2$	37°/5 mm.	1.4105	---	---	---	---	---	16.2	15.2 <sup>b</sup>
$\text{CF}_3\text{CFClNOCH}_2\text{CH}=\text{CFCHF}_2$	35°/4 mm.	1.3690	1.618	26.35	26.37	1.10	1.27	---	---

TABLE 2 (continued)

Compound	B.P. (M.P.)	$n_D^{19}$	$d_4^{22}$	% Carbon		% Hydrogen		% Halogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CF}_3\text{NOCH}_2\text{CH}=\text{CHCH}_2$	34-35°/41 mm.	1.3791	1.268	39.26	39.42	3.95	3.76	---	---
$\text{CF}_3\text{NOCH}_2\text{CH}=\text{CFCHF}_2$	41.5°/43 mm.	1.3395	---	29.01	29.31	1.45	1.49	---	---
$\text{CF}_3\text{CCl}_2\text{NOCH}_2\text{CH}=\text{CFCHF}_2$	45°/1 mm.	1.4057	---	24.85	25.02	1.04	1.18	---	---
$\text{CF}_2\text{ClCFClNOCH}_2\text{CF}=\text{CHCHF}_2$	35°/1 mm.	1.4074	---	24.85	24.75	1.04	1.24	---	---
$(\text{CF}_3)_2\text{CFNOCH}_2\text{CF}=\text{CHCHF}_2$	42°/22 mm.	1.3366	---	27.39	27.40	0.98	1.26	---	---
$\text{CF}_2\text{ClCF}_2\text{NOCH}_2\text{CF}=\text{CHCHF}_2$	49°/20 mm.	1.3635	1.604	26.35	26.28	1.10	1.27	---	---
$\text{CF}_3\text{CFClNOCH}_2\text{CF}=\text{CHCHF}_2$	45°/15 mm.	1.3686	---	26.35	26.49	1.10	0.97	---	---

TABLE 2 (continued)

Compound	B.P. (M.P.)	$n_D^{19}$	$d_4^{22}$	% Carbon		% Hydrogen		% Halogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CF}_3\text{CCl}_2\text{NOCH}_2\text{CF}=\text{CHCF}_2$	$42^\circ/1.7\text{ mm.}$	1.4074	---	24.85	25.00	1.04	1.01	---	---
				a. % Bromine		c. % Fluorine			
				b. % Chlorine		d. % Nitrogen			

## EXPERIMENTAL

All temperatures reported are uncorrected and are given in degrees Centigrade. Pressures under 10 mm. were measured by a McLeod gauge while pressures above 10 mm. were measured by a Zimmerli gauge. Refractive indices were determined with an Abbe refractometer at the temperature indicated. Densities were determined with a 1-milliliter pycnometer.

Infrared spectra were obtained using a Perkin-Elmer model 137B Infrared Spectrophotometer. Only those absorption peaks which are indicative of the structure are reported. Nuclear magnetic resonance spectra were obtained by a Varian High Resolution Nuclear Magnetic Resonance Spectrometer, model 4302 operating at 56.4 megacycles for determination of the fluorine spectra and at 60 megacycles for determination of the proton spectra. These spectra were interpreted by Dr. Wallace S. Brey, Jr., and his associates.

Analytical vapor phase chromatographs were obtained using an aluminum column 20 feet long, 0.25 inch in diameter, packed with material prepared from 0.6 gram of dinonyl phthalate per gram of Johns-Manville "Chromasorb," 35-80 mesh size. Helium was

used as the carrier gas. Preparative scale separations were performed using a glass column 8 feet long, 0.75 inch in diameter, filled with the same packing used in the analytical column.

Analyses of the two lowest boiling nitroso compounds were performed by Schwarzkopf Microanalytical Laboratory, New York; some chlorine analyses were performed by the author; all other analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Molecular weights of gases were determined by the Dumas method using a vacuum system constructed by the author.

#### A. Preparation of Mercury Alkyls

The method developed by Krespan (25) was used in preparing the mercury alkyls except that anhydrous hydrofluoric acid was used as solvent instead of arsenic trifluoride. An autoclave (1.5 liter capacity) was cooled in Dry-Ice-acetone and to it were added the mercuric fluoride, the hydrogen fluoride and the olefin. The autoclave was sealed and was rocked at the desired temperature for a specified time. The autoclave was then cooled to room temperature, vented and opened. The mercury alkyl was dissolved in ethyl ether, the ether solution was filtered and the ether was subsequently evaporated. Then the mercury alkyl was sublimed under vacuum at 85-90°. Analytical samples were resublimed.

1) Preparation of bis-(1-chloro-1,2,2,2-tetrafluoroethyl)-mercury

Chlorotrifluoroethylene (50 g., 0.43 mole), mercuric fluoride (48 g., 0.20 mole) and hydrogen fluoride (20 ml.) were placed in the autoclave. The reaction was carried out at 100° for 4 hours. Workup of the product yielded 67 g., 0.14 mole, 71 per cent yield of bis-(1-chloro-1,2,2,2-tetrafluoroethyl)mercury, m.p. 93-97°. (Krespan reported m.p. 95-97°.)

Anal. Calcd. for  $C_4Cl_2F_8Hg$ : %C, 10.2; %H, 0.00; %F, 32.2. Found: %C, 10.30; %H, 0.38; %F, 32.06.

2) Preparation of bis-(1,2,2,2-tetrafluoroethyl)mercury

Trifluoroethylene (82 g., 1.0 mole), mercuric fluoride (112 g., 0.47 mole) and hydrogen fluoride (30 ml.) were used in the reaction. The autoclave was rocked at 50° for 7 hours. Workup of the product yielded 112 g., 0.27 mole, 60 per cent yield of bis-(1,2,2,2-tetrafluoroethyl)mercury, m.p. 72-75°. (Krespan reported m.p. 78-79°.)

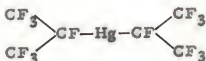
3) Preparation of bis-heptafluoroisopropylmercury

Mercuric fluoride (74 g., 0.31 mole), hexafluoropropene (100 g., 0.67 mole) and hydrogen fluoride (30 ml.) were placed in the autoclave. The autoclave was heated and rocked at 100° for 10 hours. A large quantity of the hexafluoropropene was

recovered. Workup in the usual manner resulted in a yield of 57 g., 0.032 mole, 10 per cent yield of bis-heptafluoroisopropylmercury b.p.  $35^{\circ}/26$  mm. (Krespan reported b.p. of  $116^{\circ}$  for this material.)

Anal. Calcd. for  $C_6F_{14}Hg$ : %C, 13.40; %H, 0.00; %F, 49.50; %Hg, 37.20. Found: %C, 14.24; %H, 0.94; %F, 42.83; %Hg, 38.14.

Although the analysis for fluorine was not in the proper range, a nuclear magnetic resonance spectrum of this material was consistent with the structure:



It had a peak in the  $CF_3$  region which was a doublet and another peak in the CF region which was a heptet. The relative areas of the two peaks were about 6:1. This material was also converted to the known (23) heptafluoro-2-nitrosopropane.

#### 4) Preparation of bis-(2,2,2-trifluoroethyl)mercury

Mercuric fluoride (96 g., 0.40 mole) and hydrogen fluoride (40 ml.) were placed in the autoclave and 1,1-difluoroethylene (90 g., 1.4 moles) was added to it under pressure. The reaction was carried out at  $100^{\circ}$  for 7 hours. Workup of the product resulted in a yield of 46 g., 0.18 mole, 31 per cent yield of bis-(2,2,2-trifluoroethyl)mercury, m.p.  $37-38^{\circ}$ . (Krespan reported m.p. of  $40^{\circ}$ .)



Anal. Calcd. for  $C_4H_4F_6Hg$ : %C, 13.13; %H, 1.09; %F, 31.15; %Hg, 54.64. Found: %C, 12.86; %H, 1.37; %F, 30.75; %Hg, 54.28.

5) Preparation of bis-(1,1-dichlorotrifluoroethyl)mercury

Mercuric fluoride (83 g., 0.35 mole), hydrogen fluoride (30 ml.) and 1,1-dichlorodifluoroethylene (100 g., 0.75 mole) were used. The reaction was carried out at  $125^\circ$  for 16 hours. Workup of the product yielded 110 g., 0.22 mole, 62 per cent yield of bis-(1,1-dichlorotrifluoroethyl)mercury, m.p.  $101-104^\circ$ .

Anal. Calcd. for  $C_4Cl_4F_6Hg$ : %Cl, 28.14. Found: %Cl, 24.24.

The analysis for chlorine is about half-way between that required for bis-(1,1-dichlorotrifluoroethyl)mercury and that required for 1,1-dichlorotrifluoroethylmercuric fluoride. It appears that this material is a mixture of these two compounds. The mixture was converted to 1-nitroso-1,1-dichlorotrifluoroethane, for which a correct analysis was obtained.

6) Preparation of bis-(1-bromo-1,2,2,2-tetrafluoroethyl)-mercury

Mercuric fluoride (71 g., 0.30 mole) and bromotrifluoroethylene (100 g., 0.62 mole) were used. The reaction was carried out at  $125^\circ$  for 16 hours. Workup of the product yielded

106 g., 0.19 mole, 63 per cent yield of bis-(1-bromo-1,2,2,2-tetrafluoroethyl)mercury, m. p. 53-56°.

Anal. Calcd. for  $C_4Br_2F_8Hg$ : %Br, 28.51.

Found: %Br, 28.23.

7) Attempted addition of mercuric fluoride to  
2,3-dichlorohexafluorobutene-2

Mercuric fluoride (72 g., 0.20 mole), hydrogen fluoride (30 ml.) and 2,3-dichlorohexafluorobutene-2 (145 g., 0.63 mole) were used. The reaction was carried out at 100° for 7 hours. Workup yielded only recovered starting material.

8) Addition of mercuric fluoride to 4-bromo-1,1,2-  
trifluorobutene-1

Mercuric fluoride (80 g., 0.33 mole), hydrogen fluoride (30 ml.) and 4-bromo-1,1,2-trifluorobutene-1 (130 g., 0.69 mole) were used. The reaction was carried out at 100° for 24 hours. Workup yielded 23 g. of material, m. p. 79-83°.

Anal. %C, 9.54; %H, 1.12; %F, 15.10; %Hg, 41.37.

The structure which most nearly fits the analysis is  $CH_2BrCH_2CF(CF_3)HgBr$  which requires %C, 9.83; %H, 0.82; %F, 15.6; %Hg, 41.0. The nuclear magnetic resonance spectrum of this material indicated the presence of two types of  $CF_3$  groups in a ratio of about 8:1. A CF peak which was split into at least

ten peaks was also present. An attempt to convert this material to the nitroso compound by the procedure subsequently described failed.

9) Attempted addition of mercuric fluoride to hexafluorocyclobutene

Mercuric fluoride (72 g., 0.30 mole), hydrogen fluoride (30 ml.) and hexafluorocyclobutene (101 g., 0.62 mole) were used. The reaction was carried out at 100° for 10 hours. There was recovered 88 g. of hexafluorocyclobutene. No product soluble in ether was obtained.

B. Reactions of Mercury Alkyls with Nitrosyl Chloride

The general procedure used in preparing the nitroso compounds is as follows: Dimethylformamide and the mercury alkyl were added to a 250 ml., 3-necked flask, fitted with a magnetic stirrer, a gas inlet tube and a takeoff leading to a Dry-Ice-acetone cooled condenser. Then, nitrosyl chloride was bubbled into the solution until it was dark red. The reaction proceeded very slowly, normally requiring 3 to 4 days. More nitrosyl chloride was added from time to time when the color of the solution had changed from dark red to green. Most of the nitroso compound passed into the Dry-Ice trap as it was formed. The flask was swept with nitrogen

at the end of the reaction. The product was washed twice with sodium bicarbonate to remove oxides of nitrogen and was then purified by passing it through a preparative scale vapor phase chromatographic column. This operation was necessary because the boiling point of the major impurity is very nearly the same as that of the nitroso compound.

1) Reaction of bis-(1-chloro-1,2,2,2-tetrafluoroethyl)-mercury with nitrosyl chloride

The reaction was carried out as described above using bis-(1-chlorotetrafluoroethyl)mercury (45 g., 0.095 mole), dimethylformamide (50 ml.) and excess nitrosyl chloride. There was obtained 25 g., 0.151 mole, 79 per cent yield of 1-nitroso-1-chloro-tetrafluoroethane which contained about 5 per cent 1,1-dichloro-tetrafluoroethane. The two components were separated on the preparative scale chromatographic column. The minor component, 1,1-dichlorotetrafluoroethane, was identified by comparison of its infrared spectrum with an authentic spectrum of 1,1-dichloro-tetrafluoroethane and by its nuclear magnetic resonance spectrum.

The nitroso compound has a b. p. of  $-5^{\circ}$ , determined isotoniscopically. The equation of the vapor pressure curve over the range  $-24^{\circ}$  to  $-51^{\circ}$  is  $\log p = 8.07 - 1390/T$ , the molar heat of vaporization is 6360 cal./mole and Trouton's constant is 23.8 cal./mole-deg.

Anal. Calcd. for  $C_2ONClF_4$ : %N, 8.46; %Cl, 21.43; M.W., 165.5. Found: %N, 7.65; %Cl, 20.63; M.W., 165.0.

There was also recovered from the reaction mixture a white solid, m.p. 113.5-115° (from acetic acid). This material is soluble in water, insoluble in most organic solvents and gives off an amine-like odor when dissolved in base. It was identified as  $(CH_3)_2NH_2^+HgCl_3^-$ , by its elemental analysis. It was obtained in 67 per cent yield.

Anal. Calcd. for  $C_2H_8NCl_3Hg$ : %C, 6.80; %H, 2.28; %N, 3.97; %Cl, 30.16; %Hg, 56.81. Found: %C, 6.72; %H, 2.16; %N, 3.91; %Cl, 29.99; %Hg, 56.83.

## 2) Reaction of bis-heptafluoroisopropylmercury with nitrosyl chloride

The reaction was carried out as described above using bis-heptafluoroisopropylmercury (20 g., 0.037 mole), dimethylformamide (50 ml.) and excess nitrosyl chloride. There was obtained 9.5 g., 0.048 mole, 64 per cent yield of 2-nitroso-heptafluoropropane containing less than 5 per cent impurity. After purification, a molecular weight of this material determined by the Dumas method was 199.3 (calculated for  $C_3ONF_7$ , 199.0). Its b.p., determined isoteniscopically, is -13°. (Knunyants reported b.p. -13° (23).) The vapor pressure curve is  $\log p \pm 7.58 - 1220/T$

over the temperature range  $-29^{\circ}$  to  $-77^{\circ}$ , the molar heat of vaporization is 5600 cal./mole and Trouton's constant is 21.5 cal./mole-deg.

Anal. Calcd. for  $C_3ONF_7$ : %N, 7.04; %F, 66.83.

Found: %N, 6.86; %F, 66.72.

3) Reaction of bis-(1,2,2,2-tetrafluoroethyl)mercury with nitrosyl chloride

The reaction was carried out as described previously using bis-(1,2,2,2-tetrafluoroethyl)mercury (23 g., 0.057 mole), dimethylformamide (40 ml.) and excess nitrosyl chloride. There was obtained 4 g. of a product containing four components which were separated on a preparative scale vapor phase chromatographic column. Component 1 (2 g., 14 per cent yield) was identified as 1-nitroso-1-chlorotetrafluoroethane. It had a molecular weight, determined by the Dumas method of 171 (calculated for  $C_2ONClF_4$ : 165.5; for  $C_2HONF_4$ : 131) and its b.p. was found to be  $-5^{\circ}$ . An infrared spectrum of this material is identical to that of the nitroso compound prepared from bis-(1-chlorotetrafluoroethyl)mercury and nitrosyl chloride. Furthermore, it reacted with 1,1,2-trifluorobutadiene to form a product which proved to be identical to 2-(1-chlorotetrafluoroethyl)-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [23],  $R = CF_3CFCI-$ ) as shown by elemental analysis and infrared spectra comparisons.



Component 2 was shown to be the known 1,1-dichlorotetrafluoroethane by comparison of its infrared spectrum with an authentic spectrum of 1,1-dichlorotetrafluoroethane and by its nuclear magnetic resonance spectrum.

Component 3 proved to be 1-chloro-1,2,2,2-tetrafluoroethane. It was identified by its nuclear magnetic resonance spectrum and its infrared spectrum, which contained a weak band at 3.35 microns.

Component 4 is undoubtedly a nitro compound. An infrared spectrum of this colorless material contained a strong band at 6.25 microns, characteristic of the nitro group.

4) Reaction of bis-(1,1-dichlorotrifluoroethyl)mercury with nitrosyl chloride

The procedure described above was followed using bis-(1,1-dichlorotrifluoroethyl)mercury (50.5 g., 0.10 mole), dimethylformamide (50 ml.) and an excess of nitrosyl chloride. After washing there was obtained 16 g. of a mixture containing 63 per cent 1-nitroso-1,1-dichlorotrifluoroethane and 37 per cent 1,1,1-trichlorotrifluoroethane. The yield of nitroso compound was 10 g., 0.055 mole, 28 per cent yield. A chromatographically pure sample had a b.p. of 36°, determined isoteniscopically. The vapor pressure equation is  $\log p = 7.37 - 1390/T$  over the temperature range 20° to -17°, the molar heat of vaporization is 6350 cal./mole and Trouton's constant is 20.6 cal./mole-deg.

Anal. Calcd. for  $C_2ONCl_2F_3$ : %Cl, 38.96.

Found: %Cl, 38.60.

An infrared spectrum of the second component was identical with an authentic spectrum of 1,1,1-trichlorotrifluoroethane and a nuclear magnetic resonance spectrum showed the presence of only one type of fluorine, this being present in a  $CF_3$  group.

A vapor phase chromatograph of the original mixture indicated the presence of a very small amount of higher boiling material, which is very probably 1-nitro-1,1-dichlorotrifluoroethane.

5) Reaction of bis-(2,2,2-trifluoroethyl)mercury with nitrosyl chloride

The reaction was carried out as described previously using bis-(2,2,2-trifluoroethyl)mercury (10 g., 0.027 mole), dimethylformamide (30 ml.) and excess nitrosyl chloride. No nitroso compound was obtained, nor was any low boiling material obtained.

6) Reaction of bis-(1-bromotetrafluoroethyl)mercury with nitrosyl chloride

The reaction was carried out as described previously using bis-(1-bromotetrafluoroethyl)mercury (50 g., 0.089 mole),



dimethylformamide (50 ml.) and excess nitrosyl chloride. No nitroso compound was obtained. A small amount (2 g.) of low boiling material, consisting of two major components was obtained, but was not investigated further.

### C. Rate Studies of the Disproportionation of Nitroso Compounds

The rates of disproportionation at  $78.2^{\circ}$  of four fluoro-chloro-alkyl nitroso compounds to the corresponding nitro and chloro compounds were measured. The rate of disappearance of nitroso compound was determined with a vapor phase chromatographic column using an internal standard.

The nitroso compounds were purified by passing them through a vapor phase chromatograph and were stored at  $-78^{\circ}$  until they were used.

Methylene chloride was used as internal standard for the studies of the disproportionation of 1,2-dichloro-1-nitrosotrifluoroethane and 1-nitroso-1,1-dichlorotrifluoroethane and methyl bromide was used as internal standard for the studies of the disproportionation of 1-nitroso-1-chlorotetrafluoroethane and 1-nitroso-2-chlorotetrafluoroethane. The major requirements of the internal standards were that they not react with the nitroso compounds or their disproportionation products and that their retention times on the

vapor phase chromatographic column be sufficiently different from the retention times of the nitroso compounds and their disproportionation products so that there would be no overlap of the peak with another. It was also preferable to use an internal standard whose boiling point was about the same as that of the nitroso compound. The ones chosen fulfilled these conditions.

The nitroso compound and the internal standard were mixed in the desired ratio. Aliquot portions (approximately 0.1 ml.) of the mixture were then transferred to glass tubes (5 mm. O.D., ca. 4 cm. length), which had previously been swept out with nitrogen. The tubes were sealed and were kept in Dry-Ice-acetone until they were used. For the run in which the effect of added nitric oxide upon the rate of disproportionation was determined, the tubes were filled in the usual manner. Then, nitric oxide (ca. 0.7 millimole) was added to them under vacuum and the tubes were sealed under vacuum.

The disproportionations were carried out at  $78.2 \pm 0.1^\circ$  by placing the tubes in the vapors of refluxing 95 per cent ethanol for the desired length of time. When each tube was removed it was cooled in Dry-Ice-acetone, was opened and a sample of its contents was introduced into the vapor phase chromatographic apparatus. It was necessary to maintain the vapor phase chromatographic column at a temperature at which the rate of disproportionation of nitroso

compound was negligible. The temperatures chosen for the individual nitroso compounds were:

1-nitroso-1,2-dichlorotrifluoroethane	60°
1-nitroso-1,1-dichlorotrifluoroethane	45°
1-nitroso-1-chlorotetrafluoroethane	35°
1-nitroso-2-chlorotetrafluoroethane	35°

The area under each curve was computed by multiplying the height of the peak by the width at the half-height point. This method was checked by accurately weighing a sample of methylene chloride and a sample of 1-nitroso-1,2-dichlorotrifluoroethane, mixing them and then determining the molar ratios of the two from their weights and from their areas under the curve on the vapor phase chromatograph. The results were:

	From Weights	From V.P.C.
Ratio $\frac{\text{CH}_2\text{Cl}_2}{\text{CF}_2\text{ClCFClNO}}$	2.86	2.84
	1.26	1.30

The differences in the ratios are probably due to weighing errors. The volatility of these materials is high and it was difficult to obtain accurate weights.

The results of the study are contained in Tables 3-9 and Figures 1-7.

TABLE 3

RATE OF DISPROPORTIONATION OF  
1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 78.2°

Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2}$	$\log(\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2} \times 10)$	Ratio $\frac{\text{RCl}}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RCl}}{\text{RNO}_2}$	RCl + RNO <sub>2</sub> % Total Product
0.00	2.020	1.326	none	none	---	--
0.00	1.910	1.280	none	none	---	--
0.50	1.617	1.207	---	---	---	--
1.00	1.321	1.120	---	---	---	--
1.50	1.194	1.076	0.216	0.329	0.659	76
2.00	0.950	0.976	0.272	0.352	0.775	65
3.00	0.654	0.814	0.360	0.488	0.741	68
4.00	0.454	0.656	0.434	0.578	0.752	70
5.00	0.318	0.502	0.495	0.642	0.770	71
6.25	0.206	0.312	0.525	0.637	0.827	68
7.00	0.160	0.203	0.550	0.683	0.807	70
8.00	0.118	0.069	0.694	0.871	0.794	87

$$k = 0.356 \text{ hr.}^{-1}$$

$$t_{1/2} = 1.95 \text{ hr.}$$

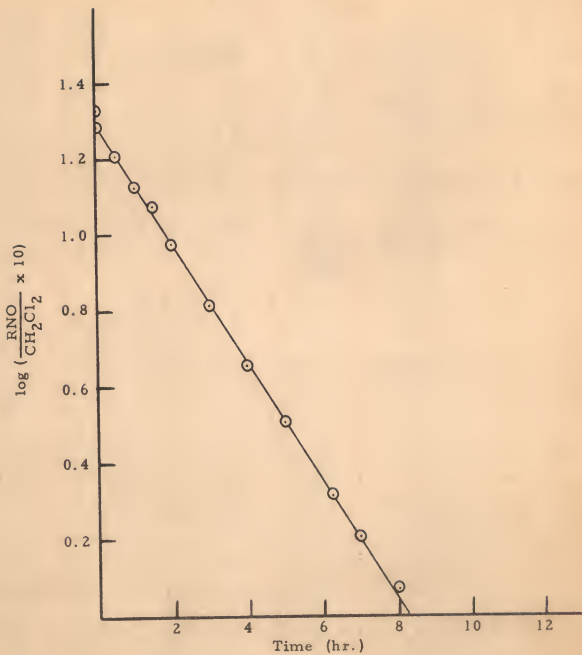


Figure 1. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane at 78.2°

TABLE 4

RATE OF DISPROPORTIONATION OF  
1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 78.2°  
IN THE PRESENCE OF ADDED NITROSYL CHLORIDE

1-Nitroso-1,2-dichlorotrifluoroethane Nitrosyl chloride			9.3 millimoles 2.1 millimoles			
Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2}$	$\log \left( \frac{\text{RNO}}{\text{CH}_2\text{Cl}_2} \times 10 \right)$	Ratio $\frac{\text{RCI}}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RCI}}{\text{RNO}_2}$	RCI + RNO <sub>2</sub> % Total Product
0.00	0.552	0.741	---	---	---	---
0.67	0.433	0.635	---	---	---	---
1.00	0.370	0.567	0.128	0.170	0.75	121
1.50	0.294	0.468	0.156	0.208	0.75	113
2.00	0.209	0.320	0.171	0.261	0.66	106
3.00	0.147	0.165	0.226	0.288	0.79	109
4.00	0.085	-0.072	0.240	0.329	0.73	107

$$k = 0.485 \text{ hr.}^{-1}$$

$$t_{1/2} = 1.43 \text{ hr.}$$

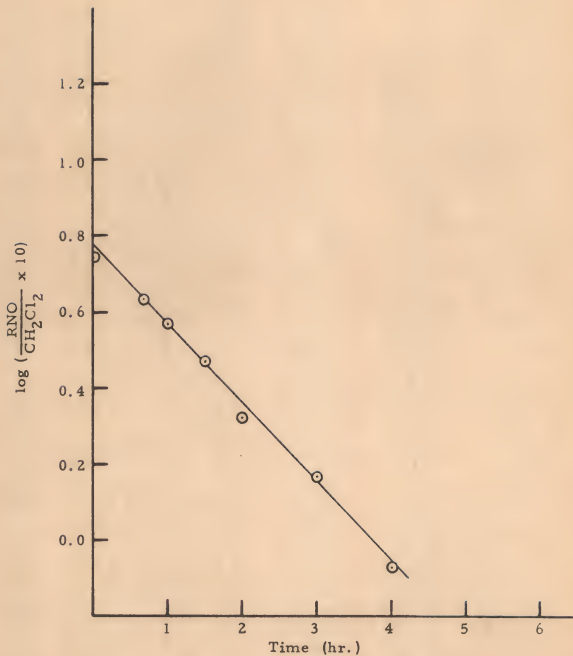


Figure 2. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane (9.3 millimoles) at 78.2° in the presence of nitrosyl chloride (2.1 millimoles)

TABLE 5

RATE OF DISPROPORTIONATION OF  
1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE  
IN THE PRESENCE OF ADDED NITRIC OXIDE

1-Nitroso-1,2-dichlorotrifluoroethane Nitric oxide			ca. 1.1 millimoles ca. 0.7 millimole		
Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2}$	$\log \left( \frac{\text{RNO}}{\text{CH}_2\text{Cl}_2} \times 10 \right)$	Ratio $\frac{\text{RCI}}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RCI}}{\text{RNO}_2}$
0.00	0.557	0.745	none	none	---
0.00	0.494	0.692	none	none	---
0.25	0.234	0.368	trace	0.356	---
0.50	0.195	0.290	0.038	0.368	---
0.75	0.159	0.200	trace	0.415	---
1.00	0.146	0.164	0.032	0.399	0.08
1.25	0.146	0.164	---	---	---
2.00	0.031	-0.503	0.060	0.496	0.12

$$t_{1/2} < 0.25 \text{ hr.}$$



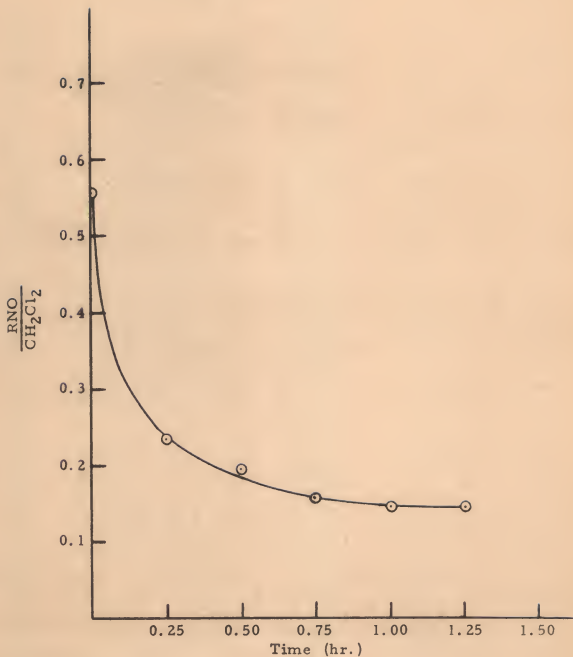


Figure 3. Concentration vs. time: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane (ca. 1.1 millimoles) at  $78.2^\circ$  in the presence of nitric oxide (ca. 0.7 millimole)

TABLE 6  
RATE OF DISPROPORTIONATION OF  
1-NITROSO-1,2-DICHLOROTRIFLUOROETHANE AT 57.0°

Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2}$	$\log \left( \frac{\text{RNO}}{\text{CH}_2\text{Cl}_2} \times 10 \right)$
0.00	1.452	1.162
4.00	1.332	1.124
8.00	1.163	1.064
12.00	1.088	1.036
16.00	1.071	1.029
20.00	0.967	0.985
24.00	0.955	0.979
28.00	0.830	0.918
32.00	0.732	0.864

$$k = 0.0205 \text{ hr.}^{-1}$$

$$t_{1/2} = 33.8 \text{ hr.}$$

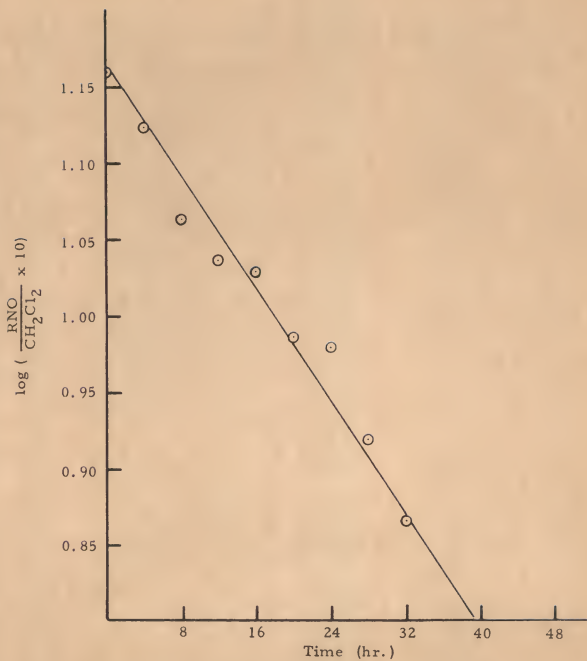


Figure 4. First order plot: disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane at 57.0°

TABLE 7

RATE OF DISPROPORTIONATION OF  
1-NITROSO-1,1-DICHLOROTRIFLUOROETHANE AT 78.2°

Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_2\text{Cl}_2}$	$\log \left( \frac{\text{RNO}}{\text{CH}_2\text{Cl}_2} \times 10 \right)$	Ratio $\frac{\text{RCI}}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_2\text{Cl}_2}$	Ratio $\frac{\text{RCI}}{\text{RNO}_2}$	RCI + RNO <sub>2</sub> % Total Product
0.00	1.130	1.052	none	none	---	---
0.25	0.927	0.966	---	---	---	---
0.50	0.883	0.945	0.212	---	---	---
1.00	0.676	0.830	0.318	---	---	---
2.00	0.392	0.592	0.566	---	---	---
2.50	0.262	0.418	0.536	---	---	---
3.00	0.230	0.361	0.619	0.288	2.15	101
4.00	0.163	0.211	0.640	---	---	---
5.00	0.085	-0.072	0.694	0.334	2.08	98
6.00	0.047	-0.329	0.482	0.234	2.06	66

$$k = 0.525 \text{ hr.}^{-1}$$

$$t_{1/2} = 1.32 \text{ hr.}$$

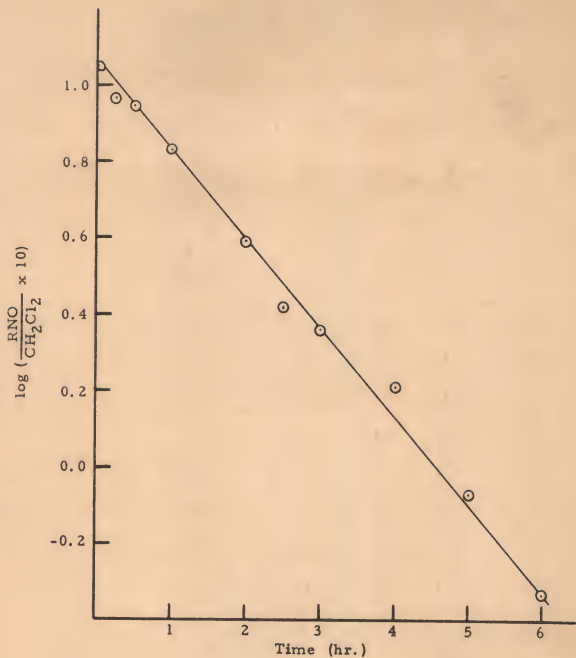


Figure 5. First order plot: disproportionation of 1-nitroso-1,1-dichlorotrifluoroethane at 78.2°C

TABLE 8

RATE OF DISPROPORTIONATION OF  
1-NITROSO-1-CHLOROTETRAFLUOROETHANE AT 78.2°

Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_3\text{Br}}$	$\log \left( \frac{\text{RNO}}{\text{CH}_3\text{Br}} \times 10 \right)$	Ratio $\frac{\text{RCI}}{\text{CH}_3\text{Br}}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_3\text{Br}}$	Ratio $\frac{\text{RCI}}{\text{RNO}_2}$	RCI + RNO <sub>2</sub> % Total Product
0.00	1.171	1.067	none	none	---	--
0.00	1.241	1.093	---	---	---	--
1.00	1.041	1.016	---	---	---	--
2.00	0.710	0.851	---	---	---	--
3.00	0.680	0.832	0.174	0.156	1.12	60
4.07	0.715	0.853	0.197	0.151	1.31	67
5.00	0.572	0.756	0.252	0.234	1.08	74
6.00	0.472	0.674	0.253	0.216	1.17	62
7.00	0.328	0.514	0.224	0.202	1.11	47
8.00	0.334	0.522	0.268	0.258	1.04	59

$$k = 0.173 \text{ hr.}^{-1}$$

$$t_{1/2} = 4.00 \text{ hr.}$$

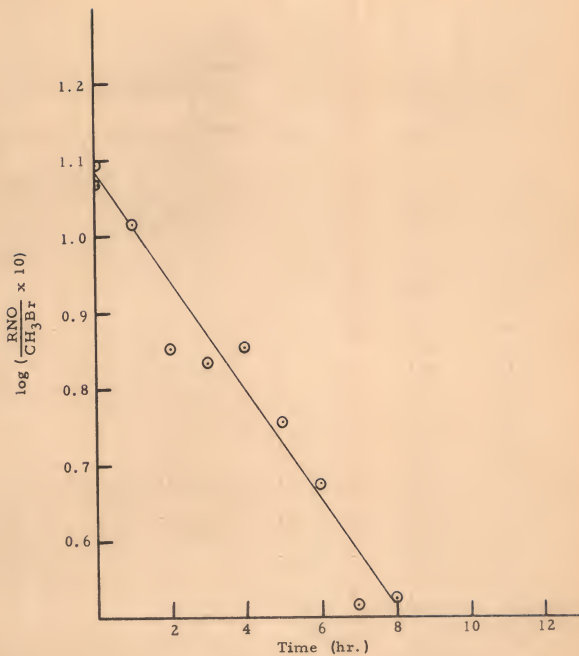


Figure 6. First order plot: disproportionation of 1-nitroso-1-chlorotetrafluoroethane at 78.2°

TABLE 9  
RATE OF DISPROPORTIONATION OF  
1-NITROSO-2-CHLOROTETRAFLUOROETHANE<sup>a</sup> AT 78.2°

Time (hr.)	Ratio $\frac{\text{RNO}}{\text{CH}_3\text{Br}}$	$\log \left( \frac{\text{RNO}}{\text{CH}_3\text{Br}} \times 10 \right)$	Ratio <sup>b</sup> $\frac{\text{RCI}}{\text{CH}_3\text{Br}}$	Ratio $\frac{\text{RNO}_2}{\text{CH}_3\text{Br}}$	$\text{RNO}_2$ % Total Product
0.00	1.062	1.025	0.257	none	---
1.00	0.931	0.968	0.259	0.184	140
2.00	0.840	0.923	0.294	0.202	91
3.00	0.843	0.924	0.236	0.195	89
4.33	0.888	0.948	0.269	0.226	130
5.00	0.786	0.895	0.218	0.195	71
6.33	0.778	0.890	0.246	0.243	86
7.04	0.749	0.873	0.229	0.235	75
10.00	0.773	0.887	0.249	0.298	103
12.00	0.739	0.868	0.241	0.303	94
17.00	0.615	0.788	0.240	0.321	72
24.00	0.555	0.743	0.238	0.452	89
30.00	0.554	0.742	0.254	0.462	71
36.75	0.533	0.725	0.262	0.560	106
42.00	0.492	0.691	0.248	0.349	61
48.00	0.425	0.628	0.267	0.480	75



TABLE 9 (continued)

Time (hr.)	Ratio RNO CH <sub>3</sub> Br	$\log \left( \frac{\text{RNO}}{\text{CH}_3\text{Br}} \times 10 \right)$	Ratio RCI CH <sub>3</sub> Br	Ratio RNO <sub>2</sub> CH <sub>3</sub> Br	RNO <sub>2</sub> % Total Product
54.00	0.467	0.668	0.264	0.345	58
60.00	0.384	0.584	0.251	0.425	63
66.00	0.346	0.538	0.243	0.412	57

$$k = 0.0141 \text{ hr.}^{-1}$$

$$t_{1/2} = 49.2 \text{ hr.}$$

- a. The author is indebted to Peninsular ChemResearch, Inc. and Dr. E. C. Stump for a sample of this material.
- b. The sample contained some 1,2-dichlorotetrafluoroethane. A second run using chromatographically pure 1-nitroso-2-chlorotetrafluoroethane showed conclusively that no 1,2-dichlorotetrafluoroethane was formed in the reaction.

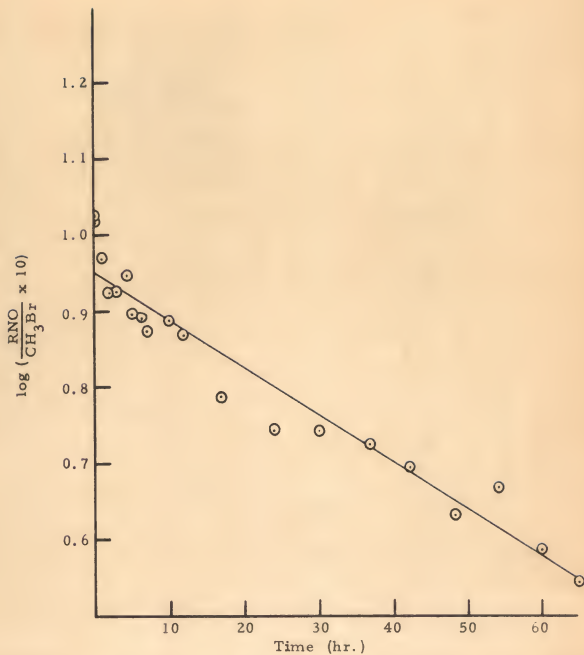


Figure 7. First order plot: disproportionation of 1-nitroso-2-chlorotetrafluoroethane at 78.2°C

#### D. Reactions of Nitroso Compounds with Dienes

The following procedure was used in the reactions of the nitroso compounds with butadiene, 1,1,2-trifluorobutadiene and 1,1,3-trifluorobutadiene. A glass tube (30 mm. O.D., 3 mm. wall, 120 ml. vol.) was swept with nitrogen and was then placed in a Dry-Ice-acetone trap. Then it was charged with the nitroso compound and the diene and was sealed. Most of the reactions ensued within 5 minutes after removal of the sealed tube from the Dry-Ice trap and within a minute or two the blue color of the nitroso compound had completely faded, indicating that the reaction was over. Then the tube was opened and the contents were distilled.

##### 1) Addition of 1,2-dichloro-1-nitrosotrifluoroethane to butadiene

Butadiene (4.5 g., 0.083 mole) and 1-nitroso-1,2-dichlorotrifluoroethane (9.0 g., 0.05 mole) were placed in the ampoule. After reaction, the material was distilled to yield 5.5 g., 0.023 mole, 47 per cent yield of 2-(1,2-dichlorotrifluoroethyl)-3,6-dihydro-1,2-oxazine (structure [21],  $R = CF_2CICFCl-$ ), b.p.  $67-68^\circ/5$  mm.

Anal. Calcd. for  $C_6H_6ONCl_2F_3$ : %Cl, 30.1.

Found: %Cl, 29.7.

This material decomposed rapidly on standing at room temperature. A nuclear magnetic resonance spectrum indicated

the presence of two types of vinyl hydrogens and two types of methylene hydrogens, present in a ratio of 1:2. The pattern of absorption peaks characteristic of a vinyl group was definitely absent. An infrared spectrum of this compound had a weak band at 5.90 microns.

2) Addition of 1-nitroso-1,2-dichlorotrifluoroethane to  
1,1,2-trifluorobutadiene

The 1,1,2-trifluorobutadiene (4.0 g., 0.050 mole) and 1-nitroso-1,2-dichlorotrifluoroethane (9.0 g., 0.050 mole) were placed in an ampoule and were allowed to react as described. Distillation yielded 2.3 g., 0.013 mole recovered 1-nitroso-1,2-dichlorotrifluoroethane, b.p. 35-40°, a second fraction weighing 4.3 g., 0.015 mole, 40 per cent yield of 2-(1,2-dichlorotrifluoroethyl)-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],  $R = CF_2ClCFC1-$ ), b.p. 35-41°/0.5 mm.,  $n_D^{19}$  1.4016,  $d_4^{22}$  1.643, and 0.75 g. of material, b.p. 70-72°/0.5 mm. which was not investigated further. There remained in the distillation flask a viscous, gummy material which was probably polymer, which was not investigated. It is noteworthy that this oxazine (fraction 2) is stable at room temperature, with no decomposition being apparent after several weeks.

Anal. of the oxazine. Calcd. for  $C_6H_3ONCl_2F_6$ :

%C, 24.85; %H, 1.04; %Cl, 24.5. Found: %C, 24.71; %H, 1.25; %Cl, 24.1.

An infrared spectrum of the material had a medium band at 5.83 microns, which is reasonable for a double bond of the type,  $-\text{CF}=\text{CH}-$ . The absence of a strong band at 5.55-5.60 microns eliminates the possibility of the presence of a trifluorovinyl group. Similarly, one would expect a band at 6.00-6.10 microns, if a vinyl group were present. A detailed analysis of a nuclear magnetic resonance spectrum of this material showed the direction of addition to be that indicated above.

Another run was carried out in which 1-nitroso-1,2-dichlorotrifluoroethane (19 g., 0.104 mole) was placed in a 250 ml., 3-necked flask and 1,1,2-trifluorobutadiene (11.0 g., 0.102 mole) was bubbled into it. Fractionation of this material yielded 21.5 g., 0.074 mole, 73 per cent yield of the oxazine, b.p.  $35-36^{\circ}/0.5$  mm.

### 3) Addition of 2-nitrosoheptafluoropropane to butadiene

Butadiene (2.0 g., 0.037 mole) and 2-nitrosoheptafluoropropane (4.0 g., 0.020 mole) were allowed to react as described previously. In this case the reaction was much slower, so the tube was allowed to stand for one hour at room temperature. Then, distillation yielded 2.0 g., 0.0079 mole, 40 per cent yield of 2-heptafluoroisopropyl-3,6-dihydro-1,2-oxazine (structure [21]),  $\text{R} = (\text{CF}_3)_2\text{CF}-$ , b.p.  $24^{\circ}/6$  mm.,  $n_D^{19}$  1.3602,  $d_4^{22}$  1.476.

Anal. Calcd. for  $C_7H_6ONF_7$ : %C, 33.23; %H, 2.39.

Found: %C, 33.30; %H, 2.56.

4) Addition of 2-nitrosoheptafluoropropane to  
1,1,2-trifluorobutadiene

2-Nitrosoheptafluoropropane (5.0 g., 0.025 mole) and 1,1,2-trifluorobutadiene (4.0 g., 0.034 mole) were kept in a sealed tube for a 9-hour period. This length of time was probably excessive, but this reaction is slower than the others of this type. Distillation yielded 5.9 g., 0.019 mole, 77 per cent yield of 2-heptafluoroisopropyl-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],  $R = (CF_3)_2CF-$ ), b.p. 21-23°/1 mm.,  $n_D^{19}$  1.3351,  $d_4^{22}$  1.771.

Anal. Calcd. for  $C_7H_3ONF_{10}$ : %C, 27.39;

%H, 0.98. Found: %C, 27.62; %H, 1.26.

5) Addition of 1-nitroso-2-chlorotetrafluoroethane to  
butadiene

Butadiene (2.1 g., 0.039 mole) and 1-nitroso-2-chlorotetrafluoroethane (4.4 g., 0.027 mole) were allowed to react as described previously. The reaction occurred at -77° while the mixture was immersed in Dry-Ice-acetone. Distillation yielded 3.9 g., 0.018 mole, 67 per cent yield of 2-(2-chlorotetrafluoroethyl)-3,6-dihydro-1,2-oxazine (structure [21],  $R = CF_2ClCF_2-$ ), b.p. 29°/3.5 mm.,  $n_D^{19}$  1.4005,  $d_4^{22}$  1.418.

Anal. Calcd. for  $C_6H_6ONClF_4$ : %Cl, 16.2.

Found: %Cl, 15.8.

6) Addition of 1-nitroso-2-chlorotetrafluoroethane to  
1,1,2-trifluorobutadiene

1-Nitroso-2-chlorotetrafluoroethane (3.7 g., 0.22 mole) and 1,1,2-trifluorobutadiene (3.0 g., 0.28 mole) were used. The reaction began while the nitroso compound was being added to the diene at  $-77^\circ$ . Distillation yielded 2.9 g., 0.011 mole, 48 per cent yield of 2-(2-chlorotetrafluoroethyl)-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],  $R = CF_2ClCF_2-$ ), b.p.  $36^\circ/4$  mm.,  $n_D^{19}$  1.3632,  $d_4^{22}$  1.610.

Anal. Calcd. for  $C_6H_3ONClF_7$ : %C, 26.35; %H, 1.10. Found: %C, 26.49; %H, 1.23.

7) Addition of 1-nitroso-1-chlorotetrafluoroethane to  
butadiene

Butadiene (2.4 g., 0.044 mole) and 1-nitroso-1-chlorotetrafluoroethane (2.0 g., 0.012 mole) were reacted as described previously. Distillation yielded 2.2 g., 0.0081 mole, 67 per cent yield of 2-(1-chlorotetrafluoroethyl)-3,6-dihydro-1,2-oxazine (structure [21],  $R = CF_3CFCl-$ ), b.p.  $37-38^\circ/5$  mm.,  $n_D^{19}$  1.4105.

Anal. Calcd. for  $C_6H_6ONClF_4$ : %Cl, 16.2.

Found: %Cl, 15.2.



This material decomposes on standing at room temperature, but does so more slowly than 2-(1,2-dichlorotrifluoroethyl)-3,6-dihydro-1,2-oxazine.

8) Addition of 1-nitroso-1-chlorotetrafluoroethane to 1,1,2-trifluorobutadiene

1-Nitroso-1-chlorotetrafluoroethane (4.0 g., 0.025 mole) and 1,1,2-trifluorobutadiene (4.0 g., 0.037 mole) were allowed to react as described previously. There was obtained from the reaction 4.8 g., 0.018 mole, 70 per cent yield of 2-(1-chlorotetrafluoroethyl)-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],  $R = CF_3CFC1-$ ), b.p.  $35^\circ/4$  mm.,  $n_D^{19}$  1.3690,  $d_4^{22}$  1.618.

Anal. Calcd. for  $C_6H_3ONClF_7$ : %C, 26.35; %H, 1.10. Found: %C, 26.37; %H, 1.27.

9) Addition of nitrosotrifluoromethane to butadiene

Butadiene (2.0 g., 0.037 mole) and nitroso-trifluoromethane (4.0 g., 0.040 mole) were introduced into a glass tube through a vacuum line. The tube was sealed under vacuum and was allowed to warm up to room temperature. There was obtained 2.7 g., 0.018 mole, 48 per cent yield of 2-trifluoromethyl-3,6-dihydro-1,2-oxazine (structure [21],  $R = CF_3-$ ), b.p.  $34.5-35^\circ/41$  mm.,  $n_D^{19}$  1.3791,  $d_4^{22}$  1.268.

Anal. Calcd. for  $C_5H_6ONF_3$ : %C, 39.26;

%H, 3.95. Found: %C, 39.42; %H, 3.76.

10) Addition of nitrosotrifluoromethane to

1,1,2-trifluorobutadiene

Nitrosotrifluoromethane (< 1.0 g.) and

1,1,2-trifluorobutadiene (2 g., 0.018 mole) were introduced into a glass tube, were sealed under vacuum and were allowed to react as described above. There was obtained 0.5 g. 2-trifluoromethyl-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],

$R = CF_3$ ), b. p.  $41.5^\circ/43$  mm.,  $n_D^{19}$  1.3395.

Anal. Calcd. for  $C_5H_3ONF_6$ : %C, 29.01;

%H, 1.45. Found: %C, 29.31; %H, 1.49.

11) Addition of the product from experimental section,

B - 3), to 1,1,2-trifluorobutadiene

1,1,2-Trifluorobutadiene (1.5 g., 0.014 mole) and product from Experimental section, B - 3), (10 g., 0.0076 mole) were allowed to react as described previously. There was obtained 1.0 g., 0.0042 mole, 55 per cent yield of the oxazine, b. p.

$49-50^\circ/10$  mm.,  $n_D^{19}$  1.3694.

Anal. Calcd. for  $C_6H_4ONF_7$ : %C, 30.15;

%H, 1.67; %Cl, 0.00. Calcd. for  $C_6H_3ONClF_7$ : %C, 26.35;

%H, 1.10; %Cl, 13.0. Found: %C, 26.37; %H, 1.45; %Cl, 12.7.

An infrared spectrum of this material was identical with an infrared spectrum of the oxazine prepared from 1-nitroso-1-chlorotetrafluoroethane and 1,1,2-trifluorobutadiene.

12) Addition of 1-nitroso-1,1-dichlorotrifluoroethane to 1,1,2-trifluorobutadiene

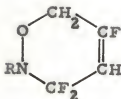
1-Nitroso-1,1-dichlorotrifluoroethane (1.0 g., 0.006 mole) and 1,1,2-trifluorobutadiene (2.0 g., 0.018 mole) were allowed to react. There was obtained 0.62 g., 0.002 mole, 33 per cent yield of 2-(1,1-dichlorotrifluoroethyl)-3,3,4-trifluoro-3,6-dihydro-1,2-oxazine (structure [24],  $R = CF_3CCl_2-$ ), b. p.  $45^\circ/1 \text{ mm.}$ ,  $n_D^{19} 1.4057$ .

Anal. Calcd. for  $C_6H_3ONCl_2F_6$ : %C, 24.85; %H, 1.04. Found: %C, 25.02; %H, 1.18.

13) Addition of 1-nitroso-1,2-dichlorotrifluoroethane to 1,1,3-trifluorobutadiene

1-Nitroso-1,2-dichlorotrifluoroethane (2.0 g., 0.011 mole) and 1,1,3-trifluorobutadiene (1.0 g., 0.009 mole) were allowed to react as described previously. There was obtained 0.70 g., 0.0024 mole, 27 per cent yield of 2-(1,2-dichlorotrifluoroethyl)-3,3,5-trifluoro-3,6-dihydro-1,2-oxazine (structure [32],  $R = CF_2ClCFCl-$ ), b. p.  $35^\circ/1 \text{ mm.}$ ,  $n_D^{19} 1.4074$ .

Anal. Calcd. for  $C_6H_3ONCl_2F_6$ : %C, 24.85; %H, 1.04. Found: %C, 24.75; %H, 1.24.



[32]

14) Addition of 2-nitrosoheptafluoropropane to  
1,1,3-trifluorobutadiene

2-Nitrosoheptafluoropropane (2.0 g., 0.010 mole) and 1,1,3-trifluorobutadiene (1.4 g., 0.013 mole) were allowed to react. There was obtained 1.3 g., 0.0042 mole, 42 per cent yield of 2-heptafluoroisopropyl-3,3,5-trifluoro-3,6-dihydro-1,2-oxazine (structure [32],  $R = (CF_3)_2CF-$ ), b.p.  $42^\circ/22$  mm.,  $n_D^{19}$  1.3366.

Anal. Calcd. for  $C_7H_3ONF_{10}$ : %C, 27.39;

%H, 0.98. Found: %C, 27.40; %H, 1.26.

15) Addition of 1-nitroso-2-chlorotetrafluoroethane to  
1,1,3-trifluorobutadiene

1-Nitroso-2-chlorotetrafluoroethane (2.0 g., 0.012 mole) and 1,1,3-trifluorobutadiene (1.4 g., 0.013 mole) were allowed to react. There was obtained 1.7 g., 0.0062 mole, 52 per cent yield of 2-(2-chlorotetrafluoroethyl)-3,3,5-trifluoro-3,6-dihydro-1,2-oxazine (structure [32],  $R = CF_2ClCF_2-$ ), b.p.  $49-51^\circ/20$  mm.,  $n_D^{19}$  1.3635,  $d_4^{22}$  1.604.

Anal. Calcd. for  $C_6H_3ONClF_7$ : %C, 26.35;

%H, 1.10. Found: %C, 26.28; %H, 1.27.

16) Addition of 1-nitroso-1-chlorotetrafluoroethane to  
1,1,3-trifluorobutadiene

1-Nitroso-1-chlorotetrafluoroethane (1.4 g., 0.0085 mole) and 1,1,3-trifluorobutadiene (2.0 g., 0.018 mole) were allowed to react. There was obtained 1.6 g., 0.0058 mole, 69 per cent yield of 2-(1-chlorotetrafluoroethyl)-3,3,5-trifluoro-3,6-dihydro-1,2-oxazine (structure [32],  $R = CF_3CFC1-$ ), b. p.  $45^\circ/15$  mm.,  $n_D^{19}$  1.3686.

Anal. Calcd. for  $C_6H_3ONClF_7$ : %C, 26.35; %H, 1.10. Found: %C, 26.49; %H, 0.97.

17) Addition of 1-nitroso-1,1-dichlorotrifluoroethane to  
1,1,3-trifluorobutadiene

1-Nitroso-1,1-dichlorotrifluoroethane (1.1 g., 0.0061 mole) and 1,1,3-trifluorobutadiene (1.5 g., 0.014 mole) were allowed to react. There was obtained 0.5 g., 0.0017 mole, 29 per cent yield of 2-(1,1-dichlorotrifluoroethyl)-3,3,5-trifluoro-3,6-dihydro-1,2-oxazine (structure [32],  $R = CF_3CCl_2-$ ), b. p.  $42^\circ/1.7$  mm.,  $n_D^{19}$  1.4074.

Anal. Calcd. for  $C_6H_3ONCl_2F_6$ : %C, 24.85; %H, 1.04. Found: %C, 25.00; %H, 1.01.

## E. Miscellaneous Reactions

### 1) Determination of the minor products from the disproportionation of 1-nitroso-1,2-dichlorotrifluoroethane

A glass tube (25 mm. O.D., 3 mm. wall) was charged with 1-nitroso-1,2-dichlorotrifluoroethane (9 g., 0.05 mole) under vacuum. The tube was sealed under vacuum and was heated at 75° for several hours. Then the tube was cooled in liquid nitrogen and was opened into the vacuum line. The pressure rose immediately indicating the presence of nitrogen. There was present 4.38 millimoles of nitrogen gas, accounting for 20 per cent of nitrogen originally present. The nitrogen was swept out and a molecular weight determination of the most volatile material remaining was 31.1 (calculated for NO: 30.0). In addition this gas became brown when exposed to the air. Thus, it is apparent that nitric oxide was also present.

Evidence for the presence of nitrosyl chloride was obtained by an examination of an infrared spectrum of the volatile gases. Bands at 5.52 and 5.59 microns, characteristic of nitrosyl chloride, were observed. In addition, the material in the tube was dark red at -78°, characteristic of nitrosyl chloride.

Another run was made similarly using 1-nitroso-1,2-dichlorotrifluoroethane (30 g., 0.16 mole). Only the high



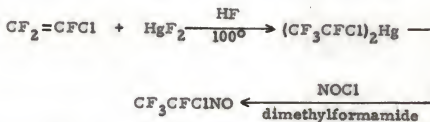
boiling material was examined. There was obtained 2.5 g. of a compound, b. p. 50-53°/23 mm. having an empirical formula of  $C_7O_5NCl_3F_7$  (Anal. %C, 19.52; %H, 0.43; %N, 3.40; %F, 32.34; %Cl, 27.3.) and a molecular weight, determined cryoscopically, of  $416 \pm 20$ . An infrared spectrum of this material contained two sharp, strong bands at 5.49 and 5.62 microns. This material hydrolyzes very slowly in distilled water to give an acidic solution.

## 2) Preparation of 1-nitroso-1,2-dichlorotrifluoroethane

This material was prepared by the method developed by Tarrant and Pisacane (37). A 500-ml., 3-necked flask was fitted with a Dry-Ice-acetone cooled condenser, a stirrer and a gas inlet tube. To it was added aluminum trichloride (23 g., 0.17 mole). Then, dimethylformamide (120 ml.) was added slowly and cautiously since a vigorous, exothermic reaction occurs between the two. Then, chlorotrifluoroethylene (1.57 g., 1.35 moles) and nitrosyl chloride (83 g., 1.27 moles) were bubbled into the stirred solution simultaneously. The reaction occurred over a 3 to 4 hour period to yield 103 g., 0.56 mole, 44.5 per cent of 1-nitroso-1,2-dichlorotrifluoroethane in 95 per cent purity. From a subsequent run carried out in the same manner there was obtained a 56 per cent yield.

## SUMMARY

The preparation of some fluoroalkyl nitroso compounds has been accomplished by a new method. An example of the two-step synthesis used is:



The reaction with mercuric fluoride occurred only with 1,1-difluoroolefins. The reaction between the fluorine-containing mercury alkyls and nitrosyl chloride was strongly dependent upon dielectric constant of the solvent. The reaction proceeded at a reasonable rate only in dimethylformamide, very slowly in diethylene glycol dimethyl ether and not at all in acetone or benzene.

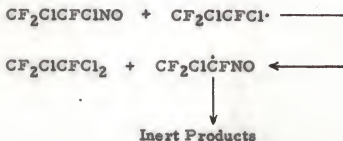
A kinetic investigation showed that the rate of disproportionation of certain fluoroalkyl nitroso compounds to the corresponding nitro and chloro compounds decreased in the following order:



The ratio of the two major products,  $\text{RCI}/\text{RNO}_2$ , decreased in the same order from a value of 2 to a value of 0.



The following mechanism is consistent with the data:



In the addition of several fluoroalkyl nitroso compounds to butadiene, 1,1,2-trifluorobutadiene and 1,1,3-trifluorobutadiene only oxazines were isolated. Nuclear magnetic resonance showed that the oxazine from 1-nitroso-1,2-dichlorotrifluoroethane and 1,1,2-trifluorobutadiene, obtained in at least 95 per cent purity, was:



This is the first report of either 1,1,2-trifluoro- or 1,1,3-trifluorobutadiene undergoing the Diels-Alder reaction. Thus, nitroso compounds appear to be extremely reactive dienophiles in this reaction.

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## BIOGRAPHICAL SKETCH

David Evans O'Connor was born April 16, 1932, at Ft. Ogden, Florida. In June, 1950, he was graduated valedictorian from Lake Placid High School. In June, 1954, he received the degree Bachelor of Science in Chemistry with high honors from the University of Florida. After graduation he entered the United States Air Force as a lieutenant and served as an Armament and Electronics Officer in the Strategic Air Command until November, 1957. Following his release from active duty, he entered the Graduate School of the University of Florida where he held a research assistantship sponsored jointly by the Office of the Quartermaster General, U.S. Army, and Wright Air Development Division, U.S. Air Force.

The author is married to the former Patricia Ann Walker and has two children. He is a member of the American Chemical Society, Gamma Sigma Epsilon and Sigma Chi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 12, 1961


  
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Dean, College of Arts and Sciences

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Dean, Graduate School

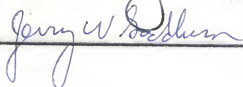
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